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MECHANISM OF COMBUSTION OF SOLID CARBON

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16. Abstract A report on measurements of temperature distribution in the reaction zone above the surface of carbon. Using a method of spectral line reversal it was found that the minimum temperature in that zone is several hundred degrees higher than that of the carbon surface.					
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The mechanism of combustion of solid carbon is still not entirely clear. On the basis of the experiments described in the literature it can be assumed as established that there are at least two or three temperature zones in which the reaction of carbon with oxygen proceeds differently. Thus it is often assumed that the reaction rate at higher temperatures is determined by diffusion processes and at lower temperatures by the surface reaction.

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However, there are still differences of opinion on the theoretical interpretation of the experiments and there are, for example, investigators who are of the opinion that at high temperatures the reaction is not governed by diffusion but by chemisorption.¹ More fundamental knowledge of the combustion mechanism is required in order to achieve further technical improvements.

Based on a study of the literature, E.F.M. van der Held² wrote a theoretical article in which special attention was devoted to the reaction zone within the gas phase in the immediate vicinity of the carbon surface, while the mechanism of the actual heterogeneous surface reaction was pretty much not considered [1]. Experiments to test this theory were begun as early as late 1960. These experiments are still in progress. However since the first measurements, which concern the temperature curve in the reaction zone, led to findings which to our knowledge have

1. Adsorption on surfaces by means of chemical valence forces.

2. Prof. van der Held is a professional consultant of the Dutch Central Technical Institute T.N.O.

* Numbers in the margin indicate pagination in the foreign text.

not yet been described, we will now report them here.

Summary of a Few Articles on the Combustion of Carbon

Although the chemical reaction of solid carbon with oxygen looks very simple on paper, in reality it turns out to be very complicated and so far no one has managed to fully clarify the mechanism. The experimental work is very difficult because many factors affecting the course of the reaction are involved in this heterogeneous reaction, such as the rate and the activation energy of the actual surface reaction, the nature of the primary reaction products, diffusion phenomena caused by the boundary layer surrounding the surface and the nature of the surface during the reaction. It is often very difficult to separate these factors experimentally. Therefore, it is also not at all surprising that on the basis of the experiment one often ends up with mutually contradictory results.

The Most Popular Measuring Techniques

The simplest measuring technique consists of burning particles of carbon or a carbon filament in a flow of gas, the composition of which is measured before and after the combustion process, while the amount of carbon burned is weighed per unit time. Naturally the temperature is also measured. This measuring technique is fairly imprecise and it provides only a general insight into the reaction.

Another method consists of burning the carbon in a flow of oxygen under very low pressure and with an adjustable flow velocity. In this way it is possible to eliminate the effect of diffusion on the reaction, while at the same time the primary reaction products can be isolated. A disadvantage of this method is that the reaction mechanism at lower pressure need not correspond to the reaction mechanism at normal pressure.

Certain tricks can also be used to study certain details of the reaction separately. Thus, for example, the afterburning of the first formed carbon monoxide to carbon dioxide can be prevented by the addition of inhibitors such as CCl_4 and PCl_3 . One can also check to what extent atomic oxygen is present in the reaction by adding NO_2 gas which produces a greenish fluorescence in the presence of O atoms.

Nevertheless, from the experimental results, which often /228 contradict themselves in particular points, a few facts can be derived which can be assumed as being established. Thus it has turned out that there are at least two and possibly even three temperature zones in which the reaction proceeds differently and therefore in which different factors determine the reaction rate. At a certain temperature, which is said to be about $1,100^\circ\text{C}$, the reaction rate is only slightly dependent on the oxygen concentration. Above this temperature, on the other hand, the reaction rate is dependent on the oxygen concentration. At temperatures above about $1,300^\circ\text{C}$ the activation energy is much smaller than at lower temperatures, i.e. the reaction rate depends to a lesser extent on the temperature.

In general it is assumed that above 800°C the primary combustion product consists almost exclusively of CO. Below this temperature, CO and CO_2 are supposed to be formed simultaneously in a ratio depends on the temperature. The experiments have also shown that the nature of the surface, the crystalline structure, the apparent and the actual density, the impurities and the hydrogen concentration may also strongly affect the reaction.

If one wants to construct a theory for the mechanism of combustion, then in any case this theory must explain these facts.

Some Recent Theories

The following two stages are distinguished in the combustion of carbon:

1. the primary reaction, i.e. a heterogeneous surface reaction during which CO and CO₂ are formed;
2. the secondary reaction, i.e. a homogeneous gas reaction during which CO combines with O₂ to form CO₂.

The first reaction is in turn determined by a number of factors: diffusion of reactive molecules to the surface of the solid phase, adsorption of gas molecules on the surface, chemical reaction in the boundary layer formed, desorption of the reaction products and diffusion of reaction products to the mass of gas.

Of these five factors the slowest process will determine the reaction rate. If the rate is nearly independent of the temperature, i.e. if the activation energy is very small, then the diffusion process is controlled. In the case of diffusion, in contrast to the situation in which chemical reactions prevail, activation energy is out of the question. If the rate depends on the temperature, then the reaction is determined either by the chemical reaction or by the adsorption and/or desorption processes. It is extremely difficult to determine experimentally which of the three last-named factors on the whole governs the reaction.

As early as 1920 it was found experimentally that the temperature coefficient of the reaction changes suddenly at a certain critical temperature. The reason for this was generally assumed to be that below this temperature the actual chemical reaction on the carbon surface determined the reaction rate, while above this temperature the overall picture was governed by diffusion. In this case the reaction rate on the surface has become so great that the diffusion rate -- which indeed in-

creases much less rapidly with increasing temperature (approximately with the square root of the temperature) then the chemical reaction rate -- is the slowest process and thus determines the overall course of the reaction.

Essenhig [2] doubts, however, that the reaction at higher temperatures is determined by the diffusion towards the carbon surface and away from the carbons surface. Instead of this, he assumes the hypothesis of oxygen chemisorption as the factor determining the reaction rate.

At temperatures above 1000°C adsorption and not diffusion is supposed to govern the reaction process. This adsorption is then to be construed as genuine chemisorption, in the process of which the oxygen is linked with chemical valences to the C atoms of the surface and not by means of the much weaker Van der Waals forces. Below this critical temperature of 1000°C desorption is supposed to govern the process. The activation energy of the desorption would then have to be much greater than that of the chemisorption, which in and of itself need not be controversial.

Wicke [3], on the basis of his experiments, came to the following conclusion: between 500 and 1,100°C both CO and CO₂ are formed, in the process of which the CO₂ portion decreases exponentially with increasing temperature and above 900°C can practically be ignored. The activation energy in this case is 25 to 30 kcal/mole. From 1,100° to 1,600°C CO is formed exclusively, while the reaction rate increases less rapidly at increasing temperatures than at temperatures below 1,100°C. Above 1,600°C only CO is produced with a reaction rate independent of the temperature.

The view is held that the explanation of all these phenomena is contained in the way in which the O atoms are bound to the lattice of the carbon atoms in solid carbon, and in the subsequent

desorption. This is thus approximately equivalent to the "chemisorption hypothesis" of Essenhig.

In a later article [4], however, transport phenomena on the carbon surface were also taken into consideration to explain the phenomena mentioned by Wicke. At temperatures below 600°C the combustion rate on the entire surface, including the pores, is determined by the heterogeneous chemical reaction. At higher temperatures (at about 750°C) the process is governed by pore diffusion, by means of which only the enveloping outer surface still participates in the reaction and consequently the activation energy is reduced by half, while at temperatures above 1,200°C the diffusion in the boundary layer next to the enveloping carbon surface determines only the reaction rate which is then almost independent of the temperature.

A similar line of thought can also be found in Khitrin [5]. In recently published experiments [6], temperatures up to 3,000°K

have been reached by high-frequency heating of spherical carbon pellets with a diameter of 15 mm, Fig. 1. The reaction of carbon with air can be explained as follows:

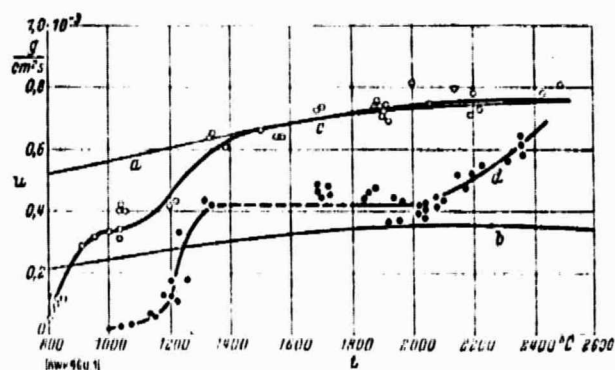


Fig. 1. Gasification rate u of carbon with air and carbon dioxide as a function of the temperature t [6].

a - calculated curve of combustion to CO governed by diffusion; b - calculated curve for combustion to CO₂ governed by diffusion; c - C + air
d - C + 50%CO₂

Above about 1,000°C the reaction is completely governed by diffusion. The fact that the reaction rate nevertheless strongly increases from 1,000° to 1,400°C is attributed to the formation of CO instead of CO₂ (thin lines in Fig. 1). At 1,400°C only CO is produced so that the reaction rate then depends on the temperature

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only to a small extent; below 1,00°C mainly CO_2 is formed. It is obvious from the lower line that the reduction of CO_2 by C at 1,100°C suddenly increases sharply.

Letrot [7] studied the mechanism of carbon combustion below 1,400°C in all its particulars. By excluding diffusion (very low pressures) he studied the mechanism of the actual surface reaction. However the results of his theory are difficult to extrapolate to the combustion experiments at normal pressure in which transport by means of diffusion is not excluded.

The Theory of Van der Held

In the theoretical consideration of Van der Held [1], in particular the gas phase reaction and the transport phenomena from and to the surface are analyzed mathematically. In this analysis the following preconditions were assumed:

1. A layer of laminar flow of sufficient thickness in the gas phase is located on the surface.
2. Combustion of carbon monoxide with externally added oxygen to carbon dioxide takes place in this layer.
3. The primary reaction product on the surface is carbon monoxide.
4. The catalytic effect of water vapor on the combustion reaction is not taken into consideration, i.e. the added combustion gas is always sufficiently moist.
5. The Boudouard equilibrium $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO} - 41.2 \text{ kcal/gmole}$ predominates on the carbon surface. This reaction is endothermic so that the required heat must be supplied by the surroundings, i.e. from the reaction zone in the gas phase, in which the reaction $\text{CO} + 1/2 \text{ O}_2 \rightarrow \text{CO}_2 + 67.6 \text{ kcal/gmole}$ takes place.

The general picture now appears as follows: in the reaction zone carbon dioxide is formed from carbon monoxide with oxygen.

Part of this carbon dioxide is transported back to the carbon surface by means of diffusion and, moreover, escapes into the surroundings (Fig. 2). The CO_2 which reaches the surface there reacts with carbon to form CO , which again is diffused away from the surface and then burns in the reaction zone to CO_2 .

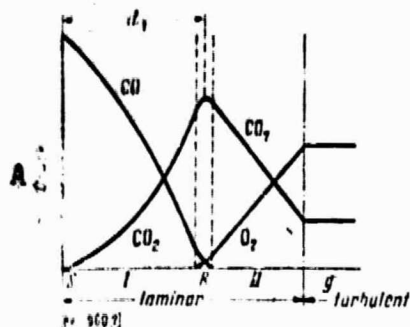


Fig. 2. Composition of the gas (partial pressures) in the laminar layer. The nitrogen pressure is not shown in the graph.

R - reaction zone; S - carbon surface; d_1 - distance from the middle of the reaction zone R to the carbon surface S; g - turbulent layer

Key: A) pressure

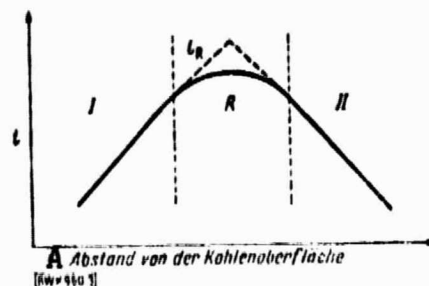


Fig. 3. The temperature distribution in the laminar layer (schematic diagram).

The maximum temperature t_R in the reaction zone R is found by extrapolating the temperature lines in zones I and II and by determining the point of intersection.

Key: A) Distance from the carbon surface

The calculations produce the following results:

The surface temperature is greater than about $1,100^\circ\text{C}$.

We imagine the gaseous reaction zone as being divided into three regions, Figs. 2 and 3:

1. The oxygen concentration and therefore also the reaction rate in the inner layer I equal zero.
2. The CO concentration and thus also the reaction rate in the outer layer II equal zero.
3. The reaction $\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2$ takes place in zone R.

It turns out that in the reaction zone R the temperatures is significantly higher than on the surface of the solid carbon.

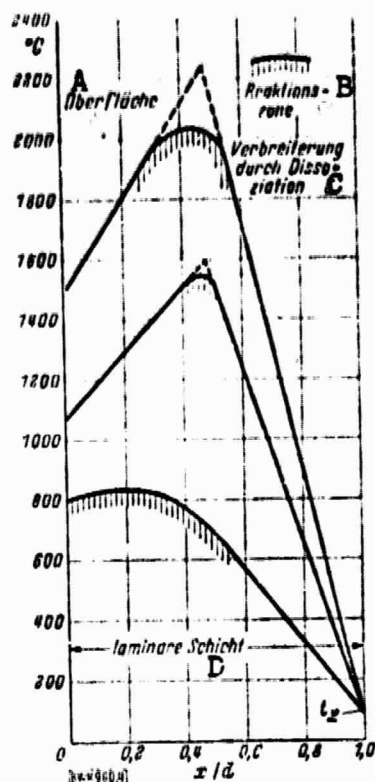


Fig. 4. The temperature distribution in the reaction zone for the combustion of carbon with air at different surface temperatures and constant air temperature t_L as a function of the ratio of the distance x from the carbon surface to the thickness d of the laminar layer.

Key:

- A) surface
- B) reaction zone
- C) increase in thickness due to dissociation
- D) laminar layer

any question or none at all of finding a maximum temperature outside the surface, Fig. 5.

By using the equations derived by Van der Held we obtain, for example at a temperature of $1,500^{\circ}\text{C}$ on the carbon surface, a maximum temperature in the zone of about $2,200^{\circ}\text{C}$, Fig. 4.

Since the thermal dissociation of molecules was not taken into consideration in the calculations, the maximum temperature in the zone will be somewhat lower than calculated.

The surface temperature is low.

At temperatures below $1,100^{\circ}\text{C}$ a certain O_2 concentration can be present on the surface.

At very low surface temperatures (below 500°C) the CO pressure on the surface is lower to such an extent that this surface is shifted into the reaction zone. The gasification of the carbon then takes place mainly, if not entirely, due to O_2 . Then there will scarcely be

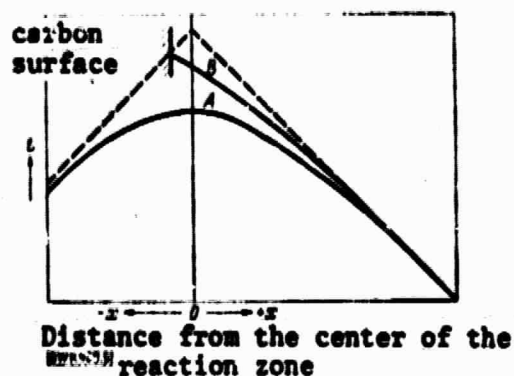


Fig. 5. Comparison of case A (free reaction zone) with Case B (disturbed reactions zone).

For measuring the temperature distribution in the reaction zone we selected the method of spectrum line reversal because it has been shown experimentally that the temperature measured in this way comes fairly close to the value of the thermodynamic temperature [8,9].

As for the term "flame temperature" it should be noted that the temperature of a gas is only clearly defined when it is in thermal equilibrium. In general, this condition is fulfilled in a diffusion flame outside the reaction zone in which the most important chemical reaction takes place. In the reaction zone, on the other hand, atoms and molecules can also be "chemically" knocked during the reaction by the formation of an activated atom or molecule in the form of an intermediate product. In this nonequilibrium state it is difficult to define the temperature, and the experimentally determined temperature depends on the measurement method used. However in the case of diffusion flames, as in our study, the measured temperature nearly agrees with the thermodynamic temperature [8;9].

In order to measure the temperature profile at a certain point in the zone the flame was colored as much as possible here and there. In our measurements we used bead of borax (sodium borate). Then a region of sodium atoms was produced around the beads in the flame, in the process of which a diffusion zone of about 1 mm thick is formed around the beads which is especially suited for measurement purposes, since the flame in this region is fairly free of disturbances.

The experiments were carried out with small carbon rods like those used for electric arcs. As everyone knows, a single solid piece of carbon cannot maintain its combustion on its own, since the loss of heat to the surroundings is too great. Therefore the experiments were carried out in a horizontal electric pipe furnace with an inside diameter of 6 cm. The pipe was set up horizontally or with a slight inclination and both ends remained opened. The carbon rod (which had been degassed beforehand) was placed in the middle of the pipe perpendicular to the pipe. The maximum achievable temperature in the furnace was about 1,200°C.

At a furnace temperature of about 700°C the carbon flared up. A clearly visible blue zone formed around the carbon. At 800°C the visible thickness of this zone was about 2.5 mm.

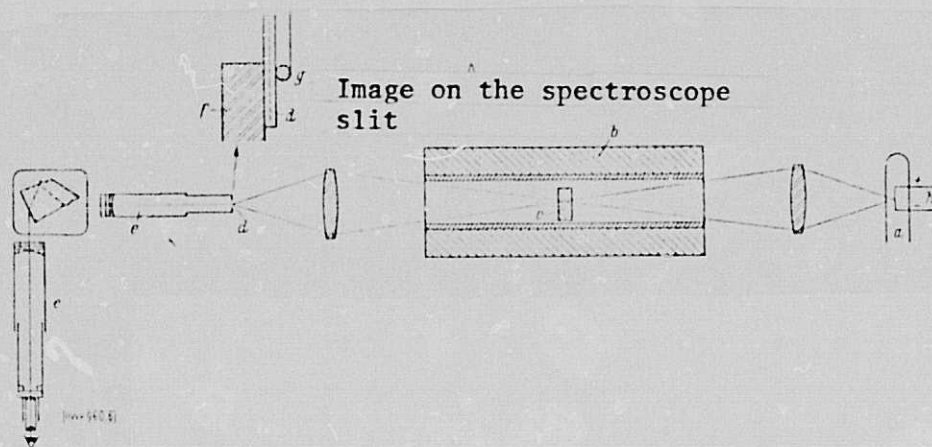


Fig. 6. Temperature measurement in the diffusion layer using the spectral line reversal method.
a - tungsten band lamp; b - electrically heated pipe furnace; c - carbon rod; d - spectroscopic slit; e - spectroscopic; f - image of the carbon rod; g - image of the borax beads; h - stabilized d.c. voltage

The temperature profile was measured in the following way (Fig. 6): the pipe furnace containing a vertical carbon rod was placed in the light path in such a way that the light passed through the pipe and the image of the light source was formed at the point of the reaction zone. In addition, the arrangement

was such that at the start of the experiment the shadow image of the carbon was just still covered by the vertical slit of the spectroscope. The borax bead was placed as close as possible to the carbon, but in such a way that the image of the bead remained outside the region of the spectroscope slit. After a short time the carbon had burned down so far that it left the slit open and consequently allowed measurements.

The moment at which the burning carbon cleared the slit was regarded as the zero point. The distance between the bead and the carbon measured at this instant was thus each time subtracted from the distances measured later. Thus neither the furnace nor the bead had to be shifted to another position during the experiment. Because of the burning down of the carbon the distance between it and the bead automatically became greater, while the image of the zone passed the spectroscope slit. By making a measurement at regular intervals of 2 to 3 minutes the temperature curve in the zone could be determined within 30 minutes up to a full hour. At the same time, the distance between the carbon and the bead was determined during each measurement.

The temperature of the surface of the carbon at the level of the bead was determined with an optical brightness pyrometer.

Experimental Results

A large number of measurements were made in the manner described. The rate at which the carbon burned down could be adjusted to some extent by somewhat changing the slight inclination of the pipe furnace. The temperature profile in the reaction zone was measured for a number of combustion rates and surface temperatures of the carbon.

Fig. 7 shows the results of three measurements at a furnace temperature of $1,000^{\circ}\text{C}$ and various burning rates Q . It is

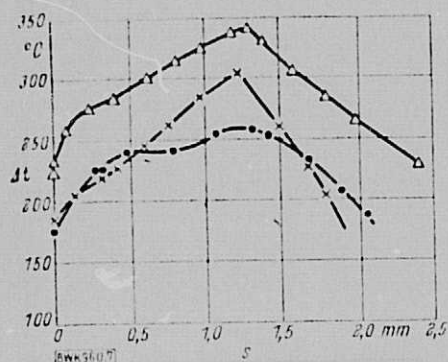


Fig. 7. Furnace temp. const.

furnace	Temp. in °C	carbon surface	Q g/h
●	1 000	995	1,6
×	1 000	1 025	6,7
Δ	1 000	1 035	8,2

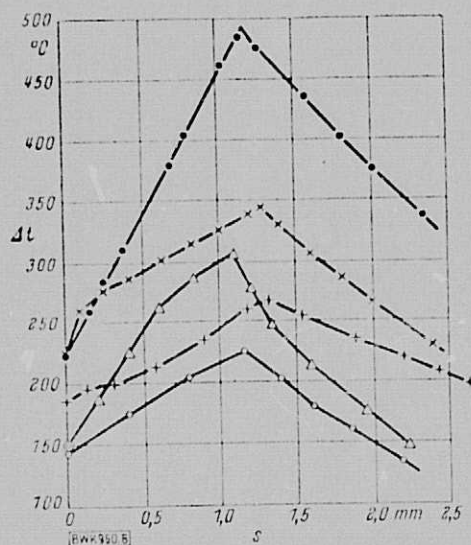


Fig. 8. Furnace Temp. varied
Temp. in °C

furnace	Temp. in °C	carbon surface	Q g/h
●	950	1 000	8,2
×	1 000	1 035	8,2
Δ	1 050	1 075	9,1
○	1 100	1 130	8,5
+	1 180	1 195	9,1

Figs. 7 and 8. The difference Δt between the maximum temperature in the reaction zone and the surface temperature of the burning carbon rod as a function of the distance s to the carbon surface.

obvious that as Q increases both the surface temperature of the carbon and the difference Δt between the maximum temperature in the reaction zone and the surface temperature of the carbon rod increase. From Fig. 8 we see that for various furnace temperatures Δt at 950°C is greater than at 1,050°C. At a furnace temperature of 1,100°C Δt decreases further, but at 1,180°C Δt again increases.

In the last two cases the peaks of the curves turn out to be much less distinct than at lower furnace temperatures. Also the reproducibility was significantly less than at temperatures below 1,100°C. Apparently a transition zone is involved above 1,100°C in which the mechanism of combustion changes, which, moreover, would agree with what is mentioned in the literature. In order to get an idea of what takes place it is necessary to carry out experiments at even higher temperatures, something this pipe furnace did not allow. In the meantime a new pipe furnace

of special construction has been ordered with which temperatures up to 2,000°C can be reached.

In addition to these temperature measurements using the line reversal method, the spectrum of the blue reaction zone was also recorded using a Hilger Medium Quartz spectrograph. The spectrum turns out to be identical with the spectrum of a carbon monoxide/air flame.

Conclusions

From what has been said above it can certainly be concluded that there is a reaction zone outside the carbon surface in which carbon monoxide burns to carbon dioxide and in which temperatures exist which can be several hundred degrees higher than the surface /231 temperature of the carbon.

This may be regarded as a qualitative confirmation of the Van der Held theory, but sufficient data are not yet available to be able to test this theory quantitatively as well. Also it is still unclear what effect the mechanism of the surface reaction exerts on the reaction zone. Therefore in the first place the measurements must be extended to the region of higher temperatures, and it also suggests itself to work at lower oxygen concentrations and total pressures which would increase the width of the reaction zone and thus facilitate the experiments. The new furnace will also offer an opportunity to do this.

In addition, measurements of CO₂ and CO concentrations inside and outside the reaction zone are necessary. This investigation is very difficult because the spectrum of a CO flame is very difficult to interpret. Perhaps it will be possible to realize the method described by Wicke [10;11] for measuring concentration by means of gas suction.

We hope to be able to report later on on the continuation of our experiments.

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